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CATALYST FOR FUEL CELL ELECTRODE
[NENRYO DENCHI DENKYOKU YO SHOKUBAI]

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Claims:

(1) A catalyst for a fuel cell electrode, said catalyst being characterized by containing alloy of platinum, nickel, and chrome.

(2) The catalyst for a fuel cell electrode, wherein said catalyst is characterized by supporting said alloy on conductive carbon.

3. Detailed Description of the Invention

[Industrial Applicable Field]

The present invention relates to a catalyst used in an electrode of a fuel cell.

[Conventional Technique]

Conventionally, a catalyst, in which platinum is supported in the form of fine particles on a carbon powder carrier, has been used as an electrochemical reaction layer of a fuel cell electrode, being kneaded with a binder such as tetrafluoroethylene fin particles. However, in case of a cathode (air electrode) of a fuel cell, in which phosphoric acid is used as an electrolyte, there are such problems that platinum in the form of fine particles gradually agglomerate during prolonged operation and cause particle growth, so that the surface area of platinum is

reduced and thereby the electromotive force of the fuel cell is reduced.

In case of an air electrode of a fuel cell, for example in case of an acid electrolyte-type fuel cell, a reaction occurs, in which oxygen in air supplied from outside the cell combines on a catalyst active metal surface such as platinum with electrons flowing in from the fuel electrode via an external circuit and protons supplied from the fuel electrode side via electrolyte inside the cell. More specifically, in the air electrode of a fuel cell, in order to rapidly proceed reduction reaction of oxygen, a catalytically active substance such as platinum is present so as to achieve the object. If the supply speed of the reaction substance is satisfactory, the reaction rate depends on the number of active sites on a catalytic substance surface.

Accordingly, prevention of reduction of the catalytically active metal surface area during use yields significant effects, and a conventional catalyst, in which only platinum is supported on a conductive carbon powder, is not always satisfactory.

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[Purpose of the Invention]

The present invention is to control the reduction of the surface area of the active metal supported on carbon powder to eliminate the defects, and thereby extend the life of the catalytic activity of the fuel cell electrode.

[Means to Solve the Problems]

The fuel cell electrode catalyst of this invention is characterized by comprising alloy of platinum, nickel, and chromium.

A reason for containing platinum, nickel, and chromium in the catalyst in this invention is to control reduction of the platinum surface area due to particle growth caused by gradual agglomeration of fine platinum particles during its use.

[Working Example]

90 g of conductive carbon black, which is thermally treated at 2,700 °C, has specific surface area of 166 m²/g by a B.E.T. method, interplanar spacing $d(002)$ of 6,748 Å, and crystallite size $L_c(002)$ of 221 Å was added in 4 L of a hexachloroplatinic acid (H₂PtCl₆) solution containing 10 g of platinum and well stirred. Then, after adding 4 L of 1.25 mol/L sodium formate (HCOONa) therein and vigorously stirring for 3 hours so as to reduce the platinum, the solution was filtered and the residue was washed. The

residue was dried in a hot-air dryer controlled at 60 °C, then further treated to dry at 120 °C in N₂ gas flow, and pulverized. As a result, 97 g of platinum-carbon was obtained.

According to chemical assay of the platinum content, the platinum content was 9.9 wt%. In addition, according to X-ray diffraction measurement, the particle diameter of the platinum was 38 Å. According to observation with an electron microscope, the platinum particles were evenly dispersed on the carbon carrier.

10 g of this platinum-carbon was dispersed in 400 mL of water, and the pH was adjusted to 8 adding dropwise an ammonium hydroxide aqueous solution. After fully stirring and dispersing, 100 mL of an aqueous solution containing 3 g of nickel in the form of nickel nitrate and 1 g of chrome in the form of chromium nitrate was added therein while stirring, and diluted nitric acid was added therein so as to adjust the pH to 5. After vigorously stirring the solution continuously for 20 minutes, the slurry was filtered, and then the residue was dried at 60 °C. Subsequently, this caked catalyst was pulverized and thermally treated in nitrogen gas flow containing 5 vol.% hydrogen at 920 °C for 3 hours. As a result, 9.4 g of a catalyst containing platinum-nickel-chromium alloy

supported on conductive carbon powder was obtained. According to x-ray diffraction, it was confirmed that platinum was alloyed differently from platinum-nickel alloy or platinum-chromium alloy. Therefore, it is considered that three-component alloy, platinum-nickel-chromium alloy, was produced. However, it was hard to determine the exact contents of nickel and chromium because of the small alloy particle size. According to results of the chemical assay, the ratio of each metal element in the alloy in the catalyst was 79 % for platinum, 15.7 % for nickel, and 5.3 % for chromium by weight ratio. A catalyst supporting the platinum-nickel-chromium alloy and tetrafluoroethylene were kneaded so as to have the ratio of 6:4, then applied on a carbon sheet treated for water repellence, and calcined so as to make an electrode. The alloy particle diameter measured by x-ray diffraction was 47 Å. Using this electrode, a half cell comprising a large amount of phosphoric acid as electrolyte was assembled, and was operated as an air electrode at 190 °C and 0.8 V for 100 hours (V. S. NHE). The alloy particle diameter measured by x-ray diffraction was 58 Å.

[Conventional Technique]

Using as a catalyst the platinum-carbon prepared in the working example, the catalyst and tetrafluoroethylene

dispersion were kneaded such that the weight ratio of the catalyst and tetrafluoroethylene was 6:4. Subsequently, the kneaded material was applied on a carbon sheet treated for water repellency, and then calcined so as to make an electrode. The diameter of platinum particles in the molded electrode, which was measured by x-ray diffraction, was 40 Å. Using this electrode, a half cell comprising a large amount of phosphoric acid as electrolyte was assembled, and then operated as an air electrode for 100 hours at 190 °C and 0.8 V (V. S. NHE). Subsequently, taking out the electrode therefrom, and the particle diameter of platinum was measured by x-ray diffraction. The particle diameter was increased to 80 Å.

In addition, using electrodes similar to those prepared in the working example and the conventional example, half cells comprising 100 % phosphoric acid as the electrolyte were respectively assembled. Oxygen was supplied from the backside of the catalytic electrode, and current was flowed between the catalytic electrode and a counter electrode. The reduction current of oxygen was measured according to a controlled-potential restriction method with a potentiostat to maintain the catalytic electrode at electric potential of 900 mV at 190 °C, using a standard hydrogen electrode disposed so as to be able to

measure electrode potential of the catalytic electrode within the same electrolyte.

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The activities of the oxygen reduction catalysts for a fuel cell can be compared by the current (mA) obtained per 1 mg platinum in the electrode at the electrode potential of 900 mV.

While the current was 28 mA/mg for a catalytic electrode supporting platinum, which is similar to the conventional example, the current of the catalytic electrode supporting a platinum-nickel-chromium alloy, which was similar to the working example, was 45 mA/mg.

As obvious from the above, the catalyst in the working example, in which platinum-nickel-chromium alloy is supported on conductive carbon powder, is effective to prevent increase of the particle diameter of the catalytic active metal particles, which significantly affects the reduction of the electromotive force of the fuel cell in comparison with a conventional catalyst comprising platinum supported on conductive carbon powder. In addition, the catalyst is also superior in the initial activity as a catalyst for an oxygen reduction electrode.

(Effects of the Invention)

As can be understood from the above description, in a catalyst for a fuel cell electrode according to this invention, the catalytic active metal particles are not platinum but platinum-nickel-chromium alloy. Therefore, the surface area reduction due to agglomeration and particle growth can be controlled even if it is used for prolonged time, so that the electromotive force hardly decreases and there is another effect of higher initial activity as an oxygen reduction catalyst due to action of nickel and chromium like promoters.